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 AB - J07228829 Aq. coating compsn. (P) contains aq. polyurethane resin (A),
 obtd. by reacting NCO gp. contg. urethane prepolymer (A1) derived from
 polyisocyanate cpd. (A1a) and 1 nonionic and/or ionic hydrophilic gp.
 or 1 gp. convertible afterwards into hydrophilic gp. contg. active
 hydrogen cpd. (A1b), with hydrazide gp.-contg. cpd. (A2) and
 polycarbonyl cpd. (B).
 - (A)/(B) solid wt. ratio is 100/0.1-0.5-100.
 - (A1a) is selected from the polyisocyanate cpds. of aromatic,
 aliphatic, alicyclic, and aromatic cyclic gps. and derivs..
 - Examples of (A1b) are tert.-amine salts of carboxylic acids, quat.
 ammonium salts, alpha,alpha'-dimethylol-alkane acids, aminosulphonic
 acids, trialkanol-amines, and diols contg. polyoxyethylene chain.
 - Opt. other active hydrogen cpds. (A1c) are used together with (A1b).
 - Examples of (A1c) are polyols having a number average molecular wt. of
 400-8,000 and polyhydric alcohols and polyamines having a molecular
 wt. of <400.
 - Examples of (A2) are dihydrazides of polycarboxylic acids,
 bis-semi-carbazides, and water-soluble acid hydrazide type polymers.
 - Examples of (B) are glyoxal, polyketones, e.g. 2,5-hexanedione and
 acetylacetone, poly-aldehydes, e.g. succinic dialdehyde and glutaric
 dialdehyde, and carbonyl gp.-contg. polymers.
 - (P) may contain additionally pigment, dispersant, and/or various
 conventional coating additives.
 - USE - (P) is used for coating various substrates, e.g. metals,
 plastics, paper, wood, cement prods., and leathers. (P) is formulated
 to undercoat, topcoat, adhesive, and/or impregnating compsns..
 - ADVANTAGE - (P) is mfd. by means of relatively simple and feasible
 processes, has good storage stability, and exhibits very slight
 toxicity. The coating films obt'd. from (P) have excellent resistance
 to water and solvents and balance of hardness and flexibility.
 - (Dwg.0/0)
 IW - AQUEOUS COATING COMPOSITION METAL PLASTIC PAPER WOOD CONTAIN
 POLYURETHANE RESIN POLY CARBONYL COMPOUND STORAGE STABILISED SLIGHT
 TOXIC
 IKW - AQUEOUS COATING COMPOSITION METAL PLASTIC PAPER WOOD CONTAIN
 POLYURETHANE RESIN POLY CARBONYL COMPOUND STORAGE STABILISED SLIGHT
 TOXIC
 NC - 001
 OPD - 1994-02-17
 ORD - 1995-08-29
 PAW - (ASAH) ASAH KASEI KOGYO KK
 TI - Aq. coating compsn. for metal, plastic, paper, wood, etc. - contains

urethane] resin and poly-carbonyl cpd., has good storage stability and only slight toxicity

A01 - [001] 017 ; G1854-R G1843 D01 F73 D10-R D13-R D18-R ; G1025-R G0997 D01 F28 F26 ; G1070-R G0997 D01 F29 F26 ; G1672-R G1649 D01 F09 F07 ; G1809-R G1649 D01 F10 F07 ; G2153-R D01 F07 D11 D10 D50 F07-R F29 F26 ; G2108-R D01 D60 F35 D11 D10 D50 F28 F26 ; G1025-R G0997 D01 F28 F26 D11 D10 D50 F34 H0204 ; D61-R F07-R F35-R ; D61-R F16 ; D61-R F07-R F62 ; G2324 D01 F11 F37 F35 F38 D60 ; G2324 D01 D23 D22 D45 F11 ; P1592-R F77 D01 ; S9999 S1025 S1014 ; H0033 H0011 ; H0259 ; H0293 ; P1581 P1570 P1592 H0260 F77 F78 D01 ; P1581 P1570 P1592 H0260 F77 F78 D01 ; H0260 ; P0931-R P1592 P0839 H0260 H0011 H0044 F41 F77 D01 D63 ; P1854 ;
- [002] 017 ; ND01 ; Q9999 Q7114-R ; K9609 K9483 ; K9563 K9483 ; K9610 K9483 ; K9541 K9483 ; K9552 K9483 ; K9574 K9483 ; K9676-R ; K9712 K9676 ; Q9999 Q6644-R ; B9999 B3532 B3372 ; B9999 B4488 B4466 ; B9999 B4706-R B4568 ; B9999 B4626 B4568 ; B9999 B3792 B3747 ; B9999 B4035 B3930 B3838 B3747 ;
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- [004] 017 ; R00823 G1503 D01 D50 D82 F22 ; A999 A157-R ;
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- [006] 017 ; R01047 D01 D11 D10 D50 D85 F23 ; A999 A157-R ;
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PATENT ABSTRACTS OF JAPAN

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(71)Applicant : ASAHI CHEM IND CO LTD

(22)Date of filing : 17.02.1994

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(54) WATER-BASED COATING COMPOSITION

(57)Abstract:

PURPOSE: To relatively easily obtain the subject composition free from any toxicity problem, excellent in storage stability, presenting adequate physical properties in terms of resistances to water and solvents even in the case of being used in an air-drying status, and in good balance between the hardness and elasticity of the coating film therefrom.

CONSTITUTION: This water-based coating composition comprises (A) a water-based polyurethane resin obtained by reaction of a hydrazide group-contg. compound with an NCO group-bearing urethane prepolymer derived from (a) a polyisocyanate compound and (b) an active hydrogen compound having nonionic and/or ionic hydrophilic group(s) (or group(s) convertible into hydrophilic group(s) afterward) and (B) a polycarbonyl compound having two or more carbonyl groups at a weight ratio A/B (on a solid basis) of (100:0.1) to (0.5:100).

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The poly isocyanate compound (a) and a non-ion system And/or, the drainage system polyurethane resin which the urethane prepolymer which has the NCO radical guided from the active hydrogen compound (b) which has an ion system hydrophilic radical (or radical which may be made to convert into a hydrophilic radical behind) was made to react with a hydrazide radical content compound, and was obtained (A), The drainage system covering constituent which consists of a Pori carbonyl compound (B) and is characterized by the solid content weight ratio being (A)/(B) = 100 / 0.1 - 0.5/100.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a drainage system covering constituent. If it says in more detail, it is useful as coating of base materials, such as a metal, plastics, paper, a tree, cement, and leather, about the covering constituent which comes to contain the drainage system polyurethane resin of cross-linking.

[0002]

[Description of the Prior Art] Drainage system polyurethane resin is excellent in film formation nature, and since the coat which has abrasion resistance, an adhesive property, rubber elasticity, etc. is given, it is used. [for the application of a coating or adhesives and a coating agent] [many] However, when using it especially with normal dry, in order not to show sufficient physical properties in points, such as a water resisting property and solvent resistance, the range used was almost restricted indoors. Moreover, the present condition is that improvement in nearby is desired in the field of the balance of a degree of hardness and elasticity.

[0003] It is useful to introduce into drainage system polyurethane resin the bridge formation system which combines cold cure nature and storage stability to these technical problems. For example, offering the self-cross-linking polyurethane emulsion in low temperature is proposed on the U.S. Pat. No. 4598121 specifications by including a hydrazide radical in a polyurethane chain and moreover adding formaldehyde. However, since it is poisonous to use formaldehyde and it is not desirable on an environment, it cannot but limit to a specific application.

[0004] On the U.S. Pat. No. 4983662 specifications, offering the polyurethane aqueosity dispersing element of self-cross-linking using the vinyl polymerization object or non-vinyl system Pori carbonyl compound which has a carbonyl functional group instead of is proposed. [said formaldehyde] However, in order to introduce a hydrazide radical in the form where it hung for the polyurethane chain according to this approach, it is difficult to introduce about [that a complicated process and a special raw material must be used] and a hydrazide radical effective in the particle front face of a polyurethane emulsion, and it does a bad influence to the weatherability of the coat which the hydrazide radical installation raw material which remains generates, a water resisting property, etc.

[0005] Moreover, in JP,1-301761,A, making a bridge construct with the vinyl polymerization object which introduces a hydrazine radical into polyurethane and has a carbonyl functional group is proposed by carrying out chain expanding of the urethane prepolymer which has a NCO radical by the hydrazine or water-soluble dihydrazine (ethylene -1, 4-JIHIDORAJIN, etc.). However, control of a reaction with a NCO radical is difficult for the hydrazine and water-soluble dihydrazine which are used by this approach a poisonous top. Therefore, the aqueosity polyurethane resin obtained is not introduced effective [a hydrazine radical] in polyurethane poisonous for the above-mentioned hydrazine derivative which remains.

[0006]

[Problem(s) to be Solved by the Invention] The polyurethane system aqueosity covering constituent obtained while the polyurethane system aqueosity covering constituent which cancels the trouble of the above-mentioned conventional technique, i.e., manufacture, was easy does not have a toxic problem, and storage stability of this invention is also good, and it is offering the polyurethane system aqueosity covering constituent which can obtain the coat which showed sufficient physical properties in points, such as a water resisting property and solvent resistance, when using it with normal dry, and was able to balance a degree of hardness and elasticity.

[0007]

[Means for Solving the Problem] By using the aqueosity covering constituent which consists of specific hydrazide radical content drainage system polyurethane resin and the specific Pori carbonyl compound, this invention persons find out that the above-mentioned trouble can be solved, and came to complete this invention. Namely, this invention The poly isocyanate compound (a) and a non-ion system And/or, the drainage system polyurethane resin which the urethane prepolymer which has the NCO radical guided from the active hydrogen compound (b) which has an ion system hydrophilic radical (or radical which may be made to convert into a hydrophilic radical behind) was made to react with a hydrazide radical content compound, and was obtained (A), It consists of a Pori carbonyl compound (B), and the solid content weight ratio is the drainage system covering constituent characterized by being $(A)/(B) = 100 / 0.1 - 0.5/100$.

[0008] Hereafter, this invention is explained in detail. As a poly isocyanate compound (a) used for compounding the urethane prepolymer which has a NCO radical in this invention For example, 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate and its mixture (TDI), Diphenylmethane 4, 4'-diisocyanate (MDI), naphthalene 1, 5-diisocyanate (NDI), The 3 and 3-dimethyl 4, 4-biphenylene di-isocyanate (TODI), Aromatic series diisocyanate, such as poor quality TDI, polymethylene polyphenyl diisocyanate, and poor quality MDI, Aromatic alicycle group diisocyanate, such as xylylene diisocyanate (XDI) and phenylene diisocyanate, 4 and 4'-methylenebis cyclohexyl diisocyanate (hydrogenation MDI), Alicycle group diisocyanate, such as isophorone diisocyanate (IPDI) and dimethylcyclohexane diisocyanate (hydrogenation XDI), diisocyanate, such as aliphatic series diisocyanate, such as hexamethylene di-isocyanate (HDI), -- further 1, a 8-G SOSHIANATO-4-isocyanato methyl octane, and a diisocyanate compound Buret association, These concomitant use, such as polyfunctional isocyanate which oligomerized by an urea bond, isocyanurate association, the urethane bond, allophanate association, urethodione association, etc., is mentioned.

[0009] Moreover, in this invention, cation radicals, such as anion radicals, such as a tertiary amine salt of a carboxylic acid, and quaternary ammonium salt, are mentioned as an ion system hydrophilic radical among the active hydrogen compounds (b) which have the non-ion system and/or ion system hydrophilic radical (or radical which may be made to convert into a hydrophilic radical behind) which are used for compounding the urethane prepolymer which has a NCO radical.

[0010] as the active hydrogen compound which has an anion radical (or radical which may be made to convert into an anion radical behind) -- alpha and alpha'-dimethylol propionic acid, and alpha and alpha - dimethylol acetic acid, and 'alpha, alpha' -- alpha, such as - dimethylol valeric acid, and a - dimethylol butanoic acid, alpha, and alpha'alpha'-dimethylol alkane -- these concomitant use, such as aminosulfonic acid, such as acids and a taurine, is mentioned. alpha and alpha'-dimethylol propionic acid is [among these] desirable. The acid radical of these active hydrogen compounds can be converted into an anion radical by neutralizing by the base at the time of composition of an urethane prepolymer, or emulsification (or aqueous-izing). As a base used for neutralization, the hydroxides of alkali metal, such as amine compounds, such as triethylamine, ammonia, diethanolamine, dimethylamino ethanol, methyldiethanolamine, and dibutyl amine, KOH, NaOH, and LiOH, and these concomitant use are mentioned, for example.

[0011] As an active hydrogen compound which has a cation radical (or radical which may be made to convert into a cation radical behind) N-alkyl dialkanolamine, such as N-methyldiethanolamine and N-butyl diethanolamine Thoria RUKANORU amines, such as triethanolamine and tripropanolamine, N, such as N,N-dimethylethanolamine and N,N-diethylethanolamine, and N-dialkyl mono-alkanolamines Moreover, these concomitant use is further mentioned for the alkylene oxide (ethylene oxide, propylene oxide, etc.) addition product of these carbon numbers 2-4 etc. The 3rd class amino group of these active hydrogen compounds can be converted into a cation radical by forming 4 class with neutralization or an alkylating agent from an acid at the time of composition of an urethane prepolymer, or emulsification (or aqueous-izing). As an acid used for neutralization, an acetic acid, a lactic acid, a hydrochloric acid, a phosphoric acid, sulfuric acids, etc. and these concomitant use are mentioned, for example. As an

alkylating agent, a dimethyl sulfate, a diethyl sulfate, methyl chloride, methyl iodide, benzyl chloride, etc. are mentioned, for example.

[0012] Moreover, as a non-ion system hydrophilic radical, the polyoxyalkylene group which hung, for example, especially a polyoxyethylene radical, etc. are mentioned. As an active hydrogen compound which has these radicals, the diol which has the polyoxyethylene chain which was indicated by the U.S. Pat. No. 3905929 specification, for example, and which solved and hung is mentioned. Moreover, as synthetic powder of this urethane prepolymer, other active hydrogen compounds (c) can be used if needed. As other active hydrogen compounds (c), the polyols of number average molecular weight 400-8000 are desirable, and it can use together the with a molecular weight of 400 or less low-molecular active hydrogen compound chosen from polyhydric alcohol and/or multiple-valued amines if needed.

[0013] As polyols of the above-mentioned number average molecular weight 400-8000, these can be used by polycarbonate polyol, polyether polyol, polyester polyol, and polybutadiene glycols according to independent or two or more sorts of concomitant use. Moreover, it is desirable to use polycarbonate polyol from points, such as a water resisting property and weatherability, in these.

[0014] The product which dihydric alcohol is made to react to the bottom of existence of a catalyst or un-existing as polycarbonate polyol with the carbonate-ized agent chosen from a phosgene, dialkyl carbonate, diaryl carbonate, and alkylene carbonate, and is obtained is mentioned. As the above-mentioned dihydric alcohol, ethylene glycol, a diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 1, 3-pentanediol, 1,6-hexanediol, etc. and two or more sorts of these concomitant use are mentioned, for example. The polycarbonate polyol obtained can be used by independent or two or more sorts of concomitant use. In these polycarbonates polyol, amorphous polycarbonate polyol which is carried by JP,2-289616,A, JP,5-25264,A, etc. from points, such as flexibility, is desirable, and the polytetramethylene carbonate diol manufactured under existence of the acid from points, such as solvent resistance and heat-resistant xanthochroism, is desirable. (For example, approach indicated by Japanese Patent Application No. No. 258748 [four to])

As an example of polyether polyol, a polyethylene glycol, a polypropylene glycol, a polytetramethylene glycol, a polyoxyethylene-oxypropylene (random and/or block) glycol, a polyoxyethylene-oxy-tetramethylen (random and/or block) glycol, a polyoxypropylene-oxy-tetramethylen (random and/or block) glycol, polyhexamethylene glycols, etc. and two or more sorts of these concomitant use are mentioned.

[0015] As an example of polyester polyol, a polyethylene horse mackerel peat, a polybutylene horse mackerel peat, a polyethylene butylene horse mackerel peat, a polybutylene hexamethylene horse mackerel peat, a polydiethylene horse mackerel peat, the Pori (polytetramethylene ether) horse mackerel peat, polyethylene azelate, polyethylene sebacate, polybutylene azelate, polybutylene sebacate, the poly caprolactone diols, etc. and two or more sorts of these concomitant use are mentioned.

[0016] As polybutadiene glycols, the polybutadiene homopolymer type which has a hydroxyl group, polybutadiene copolymer types (a styrene butadiene copolymer, acrylonitrile butadiene copolymer, etc.) the things which hydrogenated a part or all of these partial saturation double bonds, and two or more sorts of these concomitant use are mentioned to both ends.

[0017] Molecular weight usually moreover, as an example of 400 or less low-molecular active hydrogen compound For example, ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, 1,3-butanediol, 1,4-butanediol, Neopentyl glycol, 1,5-pentanediol, 1, 3-pentanediol, Dihydric alcohol, such as 1,6-hexanediol, hydrogenation bisphenol A, and cyclohexane dimethanol; A glycerol, Alcohols more than trivalent [of trimethylol propane, pentaerythritol, etc.]; Monoethanolamine, Amino alcohol, such as diethanolamine; Ethylenediamine, a hexamethylenediamine, Fatty amines, such as diethylenetriamine; alicyclic amines, such as isophorone diamine, 4, and 4-methylenebis (cyclohexylamine), etc. and two or more sorts of these concomitant use are mentioned.

[0018] This urethane prepolymer is obtained by making (c) urethane--ization-react under anhydrous conditions substantially (a), (b), and if needed at the temperature of about 30 degrees C - about 130 degrees C. This urethane prepolymer The poly isocyanate compound used in case it manufactures The NCO radical and non-ion system of (a) And/ Or an ion system hydrophilic radical () Or the radical which may be made to convert into a hydrophilic radical behind The active hydrogen compound which it has (b) () and the equivalent ratio with the active hydrogen radical (however, ion system hydrophilic radicals (or radical which may be made to convert into a hydrophilic radical behind), such as COOH, remove) which can react with the NCO radical in other active hydrogen compounds (c) if needed -- usually -- 1.1 to 5.0:1.0 -- it is 1.1 to 2.0:1.0 preferably.

[0019] In manufacture of this urethane prepolymer, if required, a catalyst can be used. As an example of a catalyst, organic tertiary amine, such as metals, such as a dibutyl tin JIRAU rate, the first tin of octylic acid, and lead octylate, organic, a salt of an inorganic acid and an organic metal derivative, triethylamine, and triethylenediamine, a diazabicycloundecen system catalyst, etc. are mentioned.

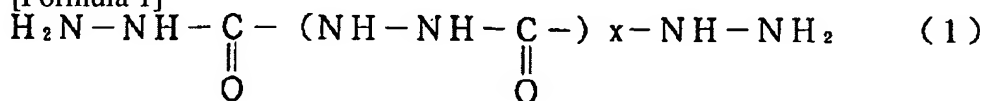
[0020] Moreover, this urethane prepolymer can be manufactured in a non-solvent or a solvent. As a solvent, it is inactive or what has activity lower than a reaction component can be used for a NCO radical. Specifically Ketone solvent; dioxanes, such as an acetone, a methyl ethyl ketone, and a methyl-isobutyl-ketone cyclohexanone, Ether system solvents, such as a tetrahydrofuran and diethylene-glycol wood ether, Lactam system solvents, such as amide system solvents, such as dimethylformamide and dimethylacetamide, and a N-methyl-2-pyrrolidone, Ester solvent, such as sulfoxide system solvents, such as dimethyl sulfoxide, ethyl acetate, and a cellosolve acetate, Aliphatic hydrocarbon system solvents, such as aromatic hydrocarbon system solvents, such as alcohols, such as t-butanol and diacetone alcohol, and a toluene xylene, and n-hexane, etc. and concomitant use of those are mentioned. In these, an acetone, a methyl ethyl ketone, and especially a N-methyl-2-pyrrolidone are desirable from points, such as emulsification dispersibility to water. Although a solvent may remain in this drainage system polyurethane resin (a polyurethane emulsion or polyurethane water solution), after considering as an emulsion (or water solution), distillation removal of it can also be heated and carried out under ordinary pressure or reduced pressure.

[0021] The drainage system polyurethane resin (A) in this invention is obtained by making the urethane prepolymer which has the NCO radical obtained by the above-mentioned approach react with a hydrazide radical content compound. this time -- the equivalent ratio of the NCO radical of this urethane prepolymer, and the active hydrogen radical of this hydrazide radical content compound -- 1.0:0.3-10.0 -- it is 1.0:1.0-2.0 preferably.

[0022] As an example of the above-mentioned hydrazide radical content compound Oxalic acid dihydrazide, malonic-acid dihydrazide, amber acid dihydrazide, Glutaric-acid dihydrazide, adipic-acid dihydrazide, sebacic-acid dihydrazide, Maleic-acid dihydrazide, fumaric-acid dihydrazide, itaconic-acid dihydrazide, Dicarboxylic acid dihydrazide, such as isophthalic acid dihydrazide and phthalic-acid dihydrazide Tricarboxylic acid TORIHIDORAJIDO, such as nitrilotriacetic acid TORIHIDORAJIDO and trimellitic acid TORIHIDORAJIDO These concomitant use (for example, indicated by JP,55-6535,A), such as a water-soluble acid hydrazide system polymer expressed with the carbonic acid dihydrazide expressed with a general formula (1), the bis-semicarbazides which are expressed with a general formula (2), and a general formula (3), is mentioned.

[0023]

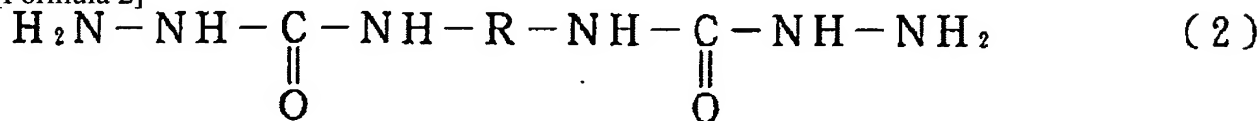
[Formula 1]



(式中 x は 0 ～ 5 の整数を意味する)

[0024]

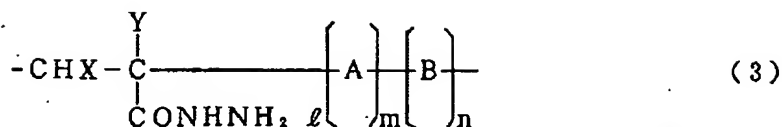
[Formula 2]



(式中 R は 2 価の直鎖状もしくは分岐状の 2 ～ 9 個の炭素原子を有する脂肪族残基または 5 ～ 8 個の炭素原子を有する脂環族残基または置換基を有しても有さなくても良い芳香族残基を表す。)

[0025]

[Formula 3]



(式中、Xは水素原子またはカルボキシル基であり、Yは水素原子またはメチル基であり、Aはアクリルアミド、メタアクリルアミド、アクリル酸エステル、メタクリル酸エステル、無水マレイン酸から選ばれる単量体の重合した単位であり、Bはアクリルアミド、メタクリルアミド、アクリル酸エステル、メタクリル酸エステル、無水マレイン酸と共重合可能な単量体の重合した単位である。

また、 l 、 m 及び n は下記の各式を満足する数を示す。

$$2 \text{ モル\%} \leq l \leq 100 \text{ モル\%}$$

$$0 \text{ モル\%} \leq m + n \leq 98 \text{ モル\%}$$

$$l + m + n = 100 \text{ モル\%}$$

[0026] It is suitable for these hydrazide radical content compounds to use the compound which has a suitable hydrophilic property. For example, adipic-acid dihydrazide, amber acid dihydrazide, sebacic acid dihydrazide, carbodihydrazide, etc. are mentioned. Moreover, use of the polyfunctional hydrazide compound containing what has hydrazide radicals, such as above-mentioned tricarboxylic acid TORIHIDORAJIDO and a water-soluble acid hydrazide system polymer, in [three or more] 1 molecule is desirable in order to make the amount of installation of the hydrazide radical to drainage system polyurethane resin increase. As occasion demands, this hydrazide radical content compound can make it able to react with a mono-aldehyde or a mono-ketone beforehand (an acetone, a methyl ethyl ketone, etc. which have the 30-200-degree C boiling point preferably), can block the at least 1 section of a hydrazide radical as a hydrazone radical, and can also be used.

[0027] as the example of the approach of making this hydrazide radical content compound reacting to this urethane prepolymer, and obtaining drainage system polyurethane resin in this invention -- ** -- the approach of adding the water solution of this hydrazide radical content compound, and making it reacting the bottom of moderate churning, and into this urethane prepolymer. ** the bottom of moderate churning, and the inside of this urethane prepolymer -- water -- adding -- as a dispersing element (or water solution) -- since -- the approach to which add the water solution of this hydrazide radical content compound, and it is made to react. ** How to add this urethane prepolymer and to make it react into the water solution of this hydrazine derivative under moderate churning. ** After making an urethane prepolymer and a hydrazide radical content compound react in a non-solvent or an organic solvent, the approach of adding water and making it into a dispersing element (or water solution) etc. is mentioned. Also in which approach of the above-mentioned ** - **, a surfactant may be added in the phase of arbitration in order to assist the dispersibility and distributed stability of this drainage system polyurethane resin as occasion demands. This surface active agent should just be [

whether it is the same ionicity radical and] nonionic when a cation system or an anion system hydrophilic group is introduced into this urethane prepolymer.

[0028] Moreover, if it is with the need, this hydrazide radical content compound can also be made to use a chain expanding agent together, in case this urethane prepolymer and this hydrazide radical content compound are made to react. As this chain expanding agent, polyethylene polyamine [, such as various diamine; diethylenetriamines], such as ethylenediamine, propylenediamine, a hexamethylenediamine, tolylenediamine, xylylene diamine, diphenyl diamine, diamino diphenylmethane, diamino cyclohexyl methane, a piperazine, 2-methyl piperazine, and isophorone diamine, and those concomitant use are mentioned, for example. Although the concentration of the pitch of the drainage system polyurethane resin (A) obtained in this way can be manufactured at 0.1 - 95wt%, manufacture top 10 - 50wt% is desirable.

[0029] Moreover, various kinds of additives for the purpose which raises weatherability etc. may be made to contain as occasion demands in manufacture of this drainage system polyurethane resin (A). the case where it reacts with reaction components, such as a case where an additive is water solubility, and an isocyanate component, although it is good to usually add at the time of composition of an urethane prepolymer when using an additive -- as a dispersing element (or water solution) -- since -- it is good to add. As an example of an additive, these concomitant use is further mentioned, for example for flameproofing agents, such as light stabilizer, such as ultraviolet ray absorbents, such as anti-oxidants, such as a hindered phenol system, a phosphite system, and a thioether system, a benzophenone system, a benzotriazol system, and a salicylate series, and a hindered amine system, and an organic halogen system, an antistatic agent, a water-repellent chemical, etc.

[0030] In this invention, when the drainage system polyurethane resin (A) and the Pori carbonyl compound (B) which were obtained by doing in this way are intermingled, functional connection is firmly discovered. It is thought that the hydrazine functional group in drainage system polyurethane resin (A), and/or a hydrazone functional group and the carbonyl group in the Pori carbonyl compound (B) produce this connection by reacting organically [in case it coat-izes].

[0031] As a Pori carbonyl compound (B), it is the compound which has two or more carbonyl groups. For example, the poly ketones, such as griot KISARU, 2,5-hexanedione, and an acetylacetone The poly aldehydes, such as guru tar dialdehyde and amber acid dialdehyde The carbonyl group content polyurethane which uses as a raw material the monochrome and/or polyalcohol which solve and have carbonyl groups, such as a hydroxy acetone, although indicated by JP,2-238015,A JP,63-51180,A, JP,62-72742,A, JP,1-13501,B, It solves, although indicated by JP,1-45497,B, JP,4-214747,A, etc.

Diacetone acrylamide, These concomitant use, such as copolymer aquosity emulsions which use carbonyl group content ethylenic unsaturated monomers, such as die acetone methacrylamide, an acrolein, a vinyl methyl ketone, and acetoacetoxylethylmethacrylate, as a copolymerization component, is mentioned. The copolymer aquosity emulsions which use a carbonyl group content ethylenic unsaturated monomer as a copolymerization component from the degree of hardness of the coat generated with the drainage system polyurethane resin (A) in this invention in these Pori carbonyl compounds (B) and Men of the balance of elasticity are desirable, and the copolymer aquosity emulsions which are made to carry out copolymerization of the carbonyl group

content ethylenic unsaturated monomer to other ethylenic unsaturated monomers under existence of a hydrolysis nature silane given in JP,4-214747,A, and are further obtained from weatherproof Men are desirable.

[0032] In this invention, the blending ratio of coal of this drainage system polyurethane resin (A) and this Pori carbonyl compound (B) requires that the solid content weight ratio should be within the limits of $(A)/(B) = 100 / 0.1 - 0.5/100$. The coat which will be generated if it deviates from this range becomes inadequate also in the balance of about [that sufficient physical properties are not shown], a degree of hardness, and elasticity in points, such as a water resisting property and alkali resistance.

[0033] A pigment, a bulking agent, a dispersant, a wetting agent, a thickener, a rheology control agent, a defoaming agent, a plasticizer, a film formation assistant, a rust-proofer, etc. can respond to each purpose as occasion demands, and the drainage system covering constituent of this invention is chosen, it can be put together and blended and can be used for various applications as a clear coat agent, a topcoat agent, a coating, an under coat agent, the impregnant of cloth or paper, various adhesives, etc.

[0034]

[Example] The section in an example means the weight section. The measuring method of each measured value used into an example is as follows. On the glass plate, the sample film (thickness is about 100 micrometers, width of face of 10mm, and die length of 60mm) used for physical-properties measurement formed membranes between five days of room temperatures, and created the drainage system covering constituent. Tensile strength was measured by part for RH, measurement length [of 30mm], and speed-of-testing/of 300mm tensilon tension tester (Cage En Tech RTA- 100) and 25 degrees-C x65% of ambient atmospheres. The water resisting property judged the sample film by the existence of milkiness of the film condition after one-week immersion with the room temperature in ion exchange water. Solvent resistance judged the sample film in the state of the film after 24-hour immersion at the room temperature in the acetone.

[0035] The example hydroxyl value of manufacture of drainage system polyurethane resin (A) put the polytetramethylene carbonate diol (C4PCDL) 1116 section of 54.6, the isophorone diisocyanate (IPDI) 363 section, the triethylamine (TEA) 55 section, the dimethylol-propionic-acid (DMPA) 73 section, the methyl-ethyl-ketone (MEK) 1607 section, and the dibutyl tin JIRAU rate (BTL) 0.04 section into the reactor which has a reflux condenser, a thermometer, and churning equipment, performed the urethane-ized reaction at 80 degrees C for 6 hours, and obtained the prepolymer solution of a NCO end. It added over about 30 minutes, agitating the adipic-acid dihydrazide water-solution 4089 section 3.5% in this prepolymer solution adjusted at 30 degrees C. Then, after removing MEK by holding as it is for 2 hours, it applies to the bottom of reduced pressure of this for 3 hours, a temperature up is carried out to 80 degrees C, ion exchange water is added, and concentration is adjusted, and they are the solid content of 30%, the viscosity (a Brookfield viscometer, 60rpm, 20 degrees C) of 16cps, and particle size 1040. The polyurethane emulsion (A-1) of pH7.8 was obtained.

[0036] By the same approach as the above, the raw material shown in Table 1 was used, and the drainage system polyurethane resin (A-2) which has the description of a publication in Table 1, and (A-3) were adjusted, respectively.

To the reactor which has the example reflux condenser of manufacture, the driptank, the thermometer, and churning equipment of the Pori carbonyl compound (B) The ion-

exchange-water 300 section, the Pelex OTP(Kao Corp. make, 40% water solution of sodium dioctyl sulfosuccinate)2 section, The emulgen 950(Kao Corp. make, 25% water solution of the polyoxyethylene nonylphenyl ether) 1 section, After supplying the dodecylbenzenesulfonic acid 1 section and raising the temperature in a reaction container to 80 degrees C Next, the mixed liquor of the five sections and the ammonium persulfate 1 section was made to flow over [driptank] 3 hours for the methacrylic-acid 11 section, the styrene 194 section, the butyl acrylate 275 section, the diacetone acrylamide 20 section, the ion-exchange-water 330 section, and emulgen 950 into a reaction container. The temperature in a reaction container was kept at 80 degrees C during the inflow. Temperature after inflow termination and in a reaction container was made into 85 degrees C, and was maintained for 6 hours. It cools to a room temperature after that, after adding an aqueous ammonia solution 25% and adjusting pH to 8, it filters at the wire gauze of 100 meshes, and they are 42.8% of solid content, and particle size 1050. The carbonyl group content copolymer aqueous emulsion (B-1) was obtained.

[0037]

[Examples 1-3, the examples 1-4 of a comparison] It was made the combination which shows drainage system polyurethane resin (A) and the Pori carbonyl compound (B) in Table 2, and the drainage system covering constituent was obtained, respectively. these constituents -- all -- 40 degrees C -- one month -- even if saved, there was almost no viscosity change and storage stability was good. The physical-properties test result of a film is shown in Table 2.

[0038]

[Table 1]

原料 (A)	A - 1	A - 2	A - 3
I P D I	3 6 3	3 6 3	3 6 3
C 4 P C D L (OH価 5 4. 6)	1 1 1 6	5 5 8	1 1 1 6
D M P A	7 3	1 1 0	7 3
T E A	5 5	8 2	5 5
B T L	0. 0 4	0. 0 4	0. 0 4
M E K	1 6 0 7	1 1 1 3	1 6 0 7
A D H 水溶液 (3. 5 w t %)	4 0 8 9	4 0 8 9	
イオン交換水			3 7 5 0
イオン交換水 (固形分調整用)	6 1 6	6 4	4 5 6
固形分 (w t %)	3 0	3 0	3 0
粘度 (c p s / 2 0 °C)	3 6	2 1 0 0	1 7
粒径 (Å)	1 0 4 0	水溶液	2 0 5 0
p H	7. 8	7. 8	8. 4

[0039]

[Table 2]

配合材料		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2	比較例 3	比較例 4
(A)	A-1 A-2 A-3	67	317	67	67	333	333	
(B)	B-1 HD ¹⁾	187	5	187	187			234
固 形 分 重 量 比 (A) / (B)		20/80	95/5	20/80	20/80	100/0	100/0	0/100
固 形 分 (wt%)		39.3	30.0	39.3	39.3	30.0	30.0	42.8
フィルムの 引張物性	100%MD ²⁾ (Kg/cm ²)	57	146	63	24	80	105	11
	破断強度 (Kg/cm ²)	224	468	256	76	213	220	18
	破断伸度 (%)	235	532	240	230	346	270	173
耐 水 性		白化しない	白化しない	白化しない	やや白化	白化	白化	やや白化
耐 溶 剤 性		変化しない	変化しない	変化しない	溶解	溶解	溶解	溶解

1) HD : 2、5-ヘキサジオン

2) 100%MD : 100%伸度モジュラス

[0040]

[Effect of the Invention] The drainage system covering constituent by this invention can obtain the coat which was able to balance a degree of hardness and elasticity while showing sufficient physical properties in points, such as a water resisting property and solvent resistance, when manufacture uses it with about [excelling in storage stability a comparatively easy top] and normal dry, so that clearly also from the above result. Therefore, the outstanding drainage system covering constituent which can be used for various applications as a clear coat agent, a topcoat agent, a coating, an under coat agent, the impregnant of cloth or paper, various adhesives, etc. is offered by this invention.

[Translation done.]